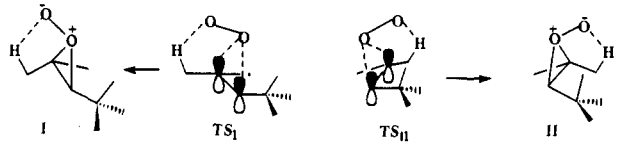
Both compounds **4** were photooxidized at 0 °C in CCl_4 with tetraphenylporphine (TPP) as sensitizer. In the ene reaction, hydrogen abstraction occurs preferentially from the trans methyl group (the less crowded side of the double bond), and the results for the *E* and *Z* isomers were the same within experimental error. This result requires that the perepoxide intermediates I and II be formed in the rate-determining step of this reaction. Similar observations, where the geminal methyl groups of the double bond do not show any significant isotope effect, have been reported earlier.[5]

Ab initio HF/STO-3G calculations[6] using full optimization showed that the cis methyl group in compound **4** has a lower rotational barrier (1.11 kcal/mol) than the trans methyl group (1.63 kcal/mol). Similar results were obtained by using the 3-21G basis.[6] In both calculations the trans methyl group in **4** has an approximately 0.5 kcal/mol higher rotational barrier than the cis methyl group. Although the "rotational barrier postulate" proposed earlier by Houk and recently by Clennan requires lower reactivity of the trans methyl than the cis methyl in compound **4**, the experimental results show the opposite. When the *tert*-butyl substituent in olefin (*E*)-**4** is replaced by an isopropyl group, producing compound **5**, the reactivity of the methyl groups has been reversed, while the rotational barriers are in the same direction as in substrate **4**. These results indicate that rotational barriers do not consistently predict the regiochemistry of this reaction.

We emphasize that in the acyclic olefins **4** the more crowded side of the olefin is the less reactive. As far as we know this is the first example in the literature where the ene reaction of an acyclic trisubstituted olefin does not obey the "cis effect". This can be attributed to the fact that in transition state TS_{II}, leading to the less stable perepoxide II, the severe nonbonded interactions involving the large *tert*-butyl group and the incoming oxygen are much larger than those in transition state TS_I, where these interactions are absent. Furthermore, unlike the "cis effect" where two allylic C–H bonds are available on the same side of the double bond, there is only one allylic C–H bond on each side of the olefinic double bond for "positive interaction" with the incoming oxygen in the transition state. Therefore no further "hydrogen stabilization" is expected in TS_{II} over TS_I. However, the more substituted side of olefin **5**, which is less hindered than in **4**, provides two C–H interactions and thus accounts for syn selectivity. Similar arguments based either on secondary orbital[7] and hydrogen-bonding interactions[8] or on activation parameters[9] have been used previously to rationalize the syn addition of singlet oxygen in trisubstituted alkenes.



Rotational barriers of the methyl groups in *cis*-, *gem*-, and *trans*-**6** compounds have also been calculated. Although the rotational barrier of the methyl group in *trans*-**6** (1.51 kcal/mol) is 3 times larger than in *cis*-**6** (0.56 kcal/mol), the reactivity of both methyl groups and consequently the regiochemistry for both substrates remain practically unchanged with both $^1O_2$ and TAD. Unlike the low reactivity of the methyl group in *cis*- and *trans*-**6** compounds, the reactivity of the methyl group in the isomer *gem*-**6** increases dramatically, while its rotational barrier has an intermediate value of 0.91 kcal/mol. These results again indicate that methyl rotations and reactivity do not correlate. Clennan and co-workers suggested that partial rotation of the neopentyl group in *cis*-**6** is sufficient to place the C–H bond in the proper orientation for abstraction.[10] According to Houk's postulate,[3] the partially rotating neopentyl group must have a lower energy barrier than 0.56 kcal/mol (the rotational barrier of the cis methyl group), in order to account for the high regioselectivity of this reaction. However, we point out that the values of the free energy of activation of ene reactions are between 6 and 13 kcal/mol for singlet oxygen[9] and >10 kcal/mol for PTAD.[5b] Since the rotational barriers of alkyl groups are much lower, the Curtin–Hammett principle[11] requires that the product ratio depend solely on the free energy difference of the transition states. The barriers to rotation are irrelevant.

A similar discrepancy between barriers to rotation and ene reactivity holds for substrate **7**. Again the cis methyl group has a lower rotational barrier than the trans although its reactivity is lower. This result again is not consonant with the interpretation that barriers to rotation dictate the regioselectivity.

The present results show that rotational barriers do not control the selectivity of the ene reaction of singlet oxygen and TAD with alkenes. We have pointed out that the regioselective ene product distribution depends on the free energy difference of the isomeric transition states. Successful prediction of product regioselectivity, therefore, requires knowledge of the structures of the pertinent isomeric transition states with alkenes.

Acknowledgment. We thank M. and S. Hourdakis Corporation, the Greek General Secretariat of Research and Technology (Grant No. ΠΣ 64), and NATO (Grant No. 880120) for financial support of the work carried out at the University of Crete. The work carried out at the University of Odense was supported by the Danish Natural Science Research Council (Grant No. 11-8487).

(5) (a) Orfanopoulos, M.; Smonou, I.; Foote, C. S. *J. Am. Chem. Soc.* **1990**, *112*, 3607–13. (b) Cheng, C. C.; Seymour, C. A.; Petti, M. A.; Greene, F. D.; Blount, J. F. *J. Org. Chem.* **1984**, *49*, 2910–6. (c) Grdina, B.; Orfanopoulos, M.; Stephenson, L. M. *J. Am. Chem. Soc.* **1979**, *101*, 3111–2.

(6) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab initio molecular orbital theory*; Wiley-Interscience: New york, 1986.

(7) Stephenson, L. M.; Grdina, M. J.; Orfanopoulos, M. *Acc. Chem. Res.* **1980**, *13*, 419–25.

(8) Bartlett, P. D.; Frimer, A. A. *Heterocycles* **1978**, *11*, 419–35.

(9) Hurst, J. R.; Wilson, S. L.; Schuster, G. B. *Tetrahedron* **1985**, *41*, 2191–7.

(10) Clennan, E. L.; Koola, J. J.; Oolman, K. A. *Tetrahedron Lett.* **1990**, 6759–62.

(11) Curtin, D. Y. *Rec. Chem. Prog.* (Kresge-Hooker Sci. Lib.) **1954**, *15*, 111. See also: Eliel, E. L. *Stereochemistry of Organic Compounds*; McGraw-Hill Book Co., Inc.: New York: 1962; Chapter 6, pp 151–6.

Synthetic Models for Catechol 1,2-Dioxygenases. Interception of a Metal Catecholate–Dioxygen Adduct

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It is generally agreed that the oxidative cleavage of catechols to *cis,cis*-muconic acids, catalyzed by non-heme iron dioxygenases, involves initial substrate binding to iron, followed by dioxygen attack at an iron(III)–catecholate complex.[1] Both the manner by which O_2 attacks the active site of the enzyme and the structural nature of the intermediate O_2 adduct are questions that may be addressed by the isolation and characterization of model compounds such as those described in this paper.

The reaction of dioxygen with the Ir(III) catecholate complexes [(triphos)Ir(Cat)]BPh_4 [Cat = 9,10-phenanthrenecatecholate (phenCat), **1**;[2] Cat = 3,5-di-*tert*-butylcatecholate (3,5-DTBCat),

(1) (a) Que, L., Jr. *Adv. Inorg. Biochem.* **1983**, *5*, 167. (b) Cox, D. D.; Que, L., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 8085. (c) Que, L., Jr. *Struct. Bonding (Berlin)* **1980**, *40*, 39.

(2) Details on the synthesis and characterization of **1** and **2** together with elemental analytical data for all of the new compounds reported in the paper are given as supplementary material.

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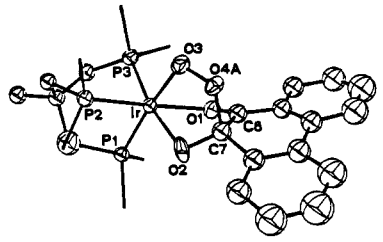
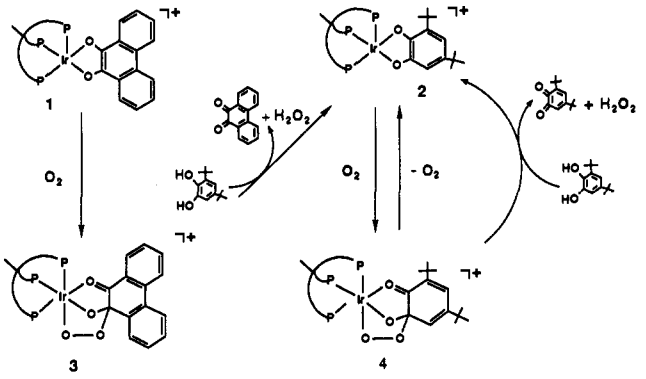


Figure 1. ORTEP drawing of the complex cation in **3**. The split image of atom O_{4A} (i.e., O_{4B}) is not shown and also the phenyl rings are omitted for clarity. The relevant geometric features are as follows (distances in angstroms; angles in degrees): Ir–P, 2.283 (22) (average); P–Ir–P, 88 (3) (average); Ir–O_1, 2.19 (1); Ir–O_2, 2.14 (1), Ir–O_3, 1.97 (1); O_1–C_6, 1.26 (2); O_2–C_7, 1.37 (2); C_6–C_7, 1.40 (2); O_3–O_{4A}, 1.47 (2); O_3–O_{4B}, 1.43 (3); C_7–O_{4A}, 1.54 (3); C_6–O_{4B}, 1.71 (4); Ir–O_3–O_{4A}, 111 (1); Ir–O_3–O_{4B}, 114 (1); O_3–O_{4A}–C_7, 110 (1); O_3–O_{4B}–C_6, 111 (2). Dihedral angle between the plane of the quinoid ligand and the equatorial P_2P_3-IrO_1O_2 plane: 25°.

Scheme I



2]^2 in CH_2Cl_2 at 25 °C results in a rapid color change of the solutions from green or violet to orange, respectively [triphos = $MeC(CH_2PPh_2)_3$]. Addition of ethanol, followed by slow evaporation of the solvents under a stream of O_2, precipitates diamagnetic orange crystals of [(triphos)Ir(OO)(phenSQ)]BPh_4·$0.5CH_2Cl_2$ (**3**) and [(triphos)Ir(OO)(3,5-DTBSQ)]BPh_4·$0.5CH_2Cl_2$ (**4**), respectively (SQ = semiquinone) (Scheme I).

The crystal structure of **3** has been determined by X-ray methods.[3] In the complex cation, the metal is octahedrally coordinated by the three phosphorus atoms of triphos and by three oxygen atoms, one from O_2 and the other two from the catecholate ligand that has attained a semiquinoid structure. The metallocycle Ir–O_3–O_{4A}–C_7–O_2 is clearly featured in Figure 1, although a disordered orientation of the oxygen molecule (based upon the refinement of site occupancy factors) allows a residual 35% probability of closing the metallocycle over the atom C_6, which is chemically equivalent to C_7. The preferential binding of the distal oxygen atom to C_7 reflects an enhancement of the incipient sp^3 hybridization at C_7 (sum of the in-plane angles: 345° at C_7 vs 358° at C_6). Analogously, the C_7 atom is more displaced than C_6 out of the catecholate plane (0.32 vs 0.09 Å). The relatively small difference excludes, however, possible macroscopic effects on the temperature factors of the two carbon atoms that could be imposed by the disordered situation. Finally, O_{4A}–C_7 [1.54 (3) Å] is shorter than the O_{4B}–C_6 bond [1.71 (4) Å] that involves a more trigonal pyramidal carbon. There are two stereocenters in each molecule (the iridium and the sp^3 carbon atom of the semiquinonate ligand) that, being interconnected, originate only two possible stereoisomers. The observed disorder suggests that an interconversion of each stereoisomer into its equivalent one is possible with the distal oxygen atom moving over the C_6–C_7 bond [1.40 (2) Å]. This interpretation is in line with the NMR information in solution, as the $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$, 298 K, 121.42 MHz) consists of a slightly second order AB_2 spin system instead of the expected ABC pattern [$\delta(P_A)$ −25.65, $\delta(P_B)$ −26.99, $J(P_AP_B)$ = 19.2 Hz]. The spectrum is temperature-invariant down to 183 K. Also, the ^1H NMR spectrum ($CDCl_3$, 298 K, 300 MHz) shows the hydrogens of the two external phenyl rings of phenSQ to constitute four equivalent pairs [$\delta(H_1)$ 8.10, $\delta(H_2)$ 7.74, $\delta(H_3)$ 7.52, $\delta(H_4)$ 7.98; $J(H_1H_2)$ = 7.90 Hz, $J(H_1H_3)$ = −0.04 Hz, $J(H_2H_4)$ = 0.64 Hz, $J(H_3H_4)$ = 7.36 Hz, $J(H_2H_3)$ = 7.99 Hz]. The ketonization of a C–O bond of the parent catecholate ligand is clearly shown by the IR spectra (Nujol mulls or $CHCl_3$ solution), which exhibit a strong ν(C=O) absorption at 1564 cm^{-1}.

The $^{31}P\{^1H\}$ NMR spectrum of **4** ($CDCl_3$, 298–183 K, 121.42 MHz), unlike that of **3**, consists of a canonical ABC spin system with $\delta(P_A)$ −25.11, $\delta(P_B)$ = 26.80, and $\delta(P_C)$ −28.84 [$J(P_AP_B)$ = 20.6 Hz, $J(P_AP_C)$ = 26.6 Hz, $J(P_BP_C)$ = 19.3 Hz]. This apparent rigidity might suggest a preferential bonding of O_2 at one of the two catecholate C–O carbon atoms. However, due to the asymmetry of the quinoid ligand, the nonequivalence of the phosphorus atoms would be observable also for a fast equilibrium involving shuttling back and forth of the oxygen atom between the two C–O carbon atoms. The two *tert*-butyl substituents are evidently inequivalent, as shown by the ^1H NMR (CD_2Cl_2, 298 K, 300 MHz) spectrum, which contains two singlets (9 H) at 1.37 and 1.34 ppm. Finally, the presence of a C=O group coordinated to iridium via the oxygen atom is put in evidence by a strong IR absorption at 1538 cm^{-1}.

In spite of their having the same primary geometry, **3** and **4** have different stabilities in solution. Complex **3** is thermally stable at 100 °C in CH_3NO_2 even in anaerobic conditions, whereas **4** begins to lose O_2 converting into **2** at 35 °C even under a dioxygen atmosphere. Also, bubbling N_2 through a room temperature solution of **4** converts the complex into the precursor **2** and O_2. The rate of the conversion significantly depends on the intensity of the N_2 stream. The process is reversible, thus showing the ability of the system to act as a versatile oxygen carrier, the uptake/release being controlled by small variations of either the temperature or the partial pressure of O_2.

Compound **3** reacts with a stoichiometric amount of 3,5-di-*tert*-butylcatechol in CH_3NO_2 at 90 °C, converting to **2** and producing phenanthrenequinone and H_2O_2. In turn, the latter complex in CH_2Cl_2 catalyzes under very mild conditions the reaction between O_2 and 3,5-di-*tert*-butylcatechol to give selectively H_2O_2 (determined by iodometry) and 3,5-di-*tert*-butyl-*o*-benzoquinone (20 °C; substrate to catalyst ratio 100; 24 h; 37% conversion).[4]

The isolation and characterization of **3** and **4** is thought provoking relative to the process of O_2 activation and binding by the dioxygenase enzyme. In this respect, it is noteworthy that, according to a recent model study,[1b] an intermediate species in the catalysis cycle could be an iron peroxide complex exhibiting close structural analogies with **3** and **4**. Actually, our complexes are not able to catalyze the C–C cleavage of catechols. However, this may be due to the nature of the metal center. As a matter of fact, just by replacing iridium with rhodium, viz., using [(triphos)-Rh(3,5-DBCat)]BPh_4 as the O_2 activating system, both intradiol and extradiol ring cleavage of 3,5-di-*tert*-butylcatechol has been observed.[4]

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Supplementary Material Available: Experimental details for the syntheses of **1** and **2**, spectroscopic and microanalytical data for **1**–**4**, and X-ray crystallographic data for **3** including exper-

(3) Triclinic crystal, space group $P\bar{1}$, a = 10.794 (4) Å, b = 16.679 (5) Å, c = 19.586 (3) Å, α = 84.94 (2)°, β = 76.79 (2)°, γ = 78.93 (2)°, MW = 1418.71, Z = 2, d_{calcd} = 1.43 g cm^{-3}, μ(Mo Kα) = 21.2 cm^{-1}, 9495 measured reflections of which 5548 were unique [$I > 3\sigma(I)$]. An overall decay of ca. 10% was observed for a chosen set of standard reflections. In the least-squares refinement Ir, P, and O atoms were assigned anisotropic temperature factors and the phenyl rings were treated as rigid bodies. The final R and R_w factors have the same value of 0.065. A final ΔF map is essentially featureless.

(4) Bianchini, C.; Frediani, P.; Laschi, F.; Meli, A.; Vizza, F.; Zanello, P. *Inorg. Chem.* **1990**, *29*, 3402.

imental details, atomic coordinates and thermal parameters, and selected distances and angles (7 pages); listing of observed and calculated structure factors for **3** (31 pages). Ordering information is given on any current masthead page.

Reversible Generation of Trimethylenemethanes by Mild Thermolysis of Dialkoxymethylenecyclopropanes

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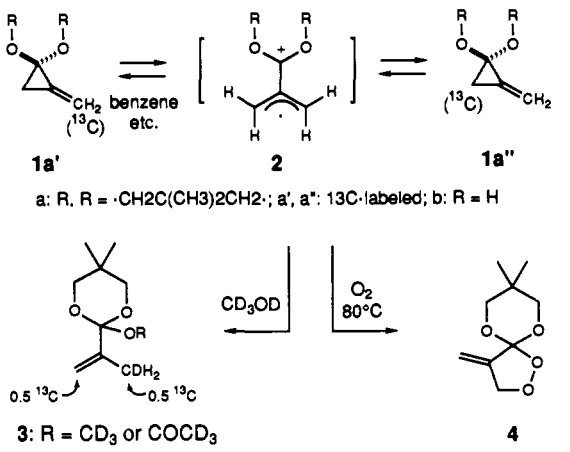
Trimethylenemethane (TMM) is a uniquely important diradical species that has long attracted the interest of chemists.[1] Thermolysis of methylenecyclopropanes (MCPs) should provide a simple entry to the TMMs, and indeed we find many such allusions in the literature.[2] However, to date no direct evidence for the formation of a discrete TMM has been obtained,[3] except for the thermolysis of a strained [2.1.0] bicyclic skeleton.[4] We now report the first direct experimental evidence that *reactive TMM species can be generated thermally and reversibly from simple monocyclic MCPs*. We also describe ab initio theoretical studies on a model species.

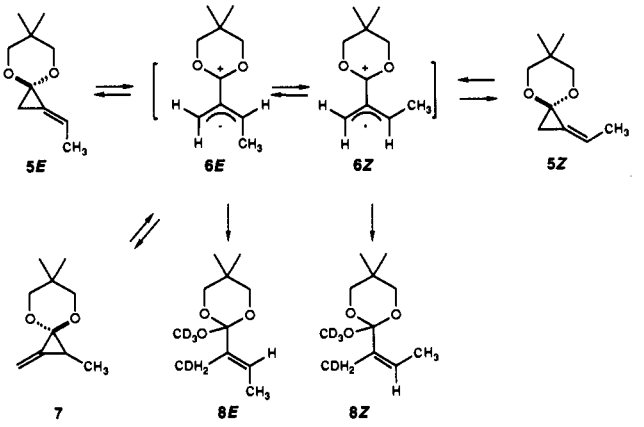
The specific MCP under study is the dialkoxy MCP **1a**, which has apparent thermal stability (100 °C, 24 h, toluene), yet undergoes thermal [3 + 2] cycloadditions.[5] Initial information on the dynamic properties of **1a** was gained by the observation of the facile thermal rearrangement of **1a'**[6] (the *exo*-methylene carbon is ^{13}C labeled) to **1a''**, which now bears the ^{13}C label on the ring carbon (Scheme I). The isomerization proceeded rapidly at 40–70 °C, producing a 1:1 mixture of **1a'** and **1a''**.[7] The first-order rate constant (k) of the reaction (60 °C, C_6D_6: 0.30 M solution throughout the studies) was 9.6×10^{-5} s^{-1}, and the activation energy (E_a) was 25.5 kcal/mol (50–70 °C), a value much lower than that for the unsubstituted MCP.[8] The E_a of the rearrangement in CD_3CN was 22.2 kcal/mol ($k = 6.0 \times 10^{-4}$ s^{-1}, 60 °C). The rate (60 °C) increased by a factor of 191 as the solvent was changed from C_6D_{12} (5.7×10^{-6} s^{-1}) to DMSO-d_6 (1.1×10^{-3} s^{-1}), suggesting a relatively polar transition state. The rate of the rearrangement of **1a'** changed little in the presence of 1,4-dinitrobenzene (1 equiv, a radical trap) or under 1 atm of oxygen. However, bubbling oxygen into a heated toluene solution of **1a** (80 °C, 24 h) effect slow conversion of **1a** to an unstable peroxide **4** (40%).[9] In no cases did we observe CIDNP signals during the NMR analyses.[10]

Direct evidence for the TMM **2a** was obtained by solvolysis of **1a'** in deuterated acidic solvents. Thus, the reaction of **1a'** in CD_3COOD or CD_3OD at 40–60 °C gave an ortho ester **3** in quantitative yield, *wherein a deuterium was specifically found on the allylic methyl group with complete scrambling of the ^{13}C label whereas the label in **1a'** remained intact throughout the reaction*, indicating that the "memory" of the labeling in **1a'** was lost at a D^+ quenching stage.[11] No products due to $D^\bullet$ abstraction from the CD_3 group of the solvent were observed. Hydrolysis of **1a'** in DCl/D_2O also proceeded quantitatively with complete ^{13}C scrambling. The pseudo-first-order rate constant of the methanolysis of **1a** at 60 °C was 1.1×10^{-3} s^{-1} with E_a = 24.9 kcal/mol

Scheme I



Scheme II



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§ Institute for Molecular Science.

(1) (a) Theory: Feller, D.; Tanaka, K.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1982**, *104*, 967 and references therein. (b) Physical organic chemistry: Weiss, F. *Q. Rev., Chem. Soc.* **1970**, *24*, 1970. Dowd, P. *Acc. Chem. Res.* **1972**, *5*, 242. Dowd, P.; Chow, M. *Tetrahedron* **1982**, *38*, 799. See also ref 10b. (c) Synthesis: Little, R. D. *Chem. Rev.* **1986**, *86*, 875. Welzel, P. *Nachr. Chem., Tech. Lab.* **1983**, *31*, 638. (d) Organometallics: Jones, M. D.; Kemmitt, R. D. W. *Adv. Organomet. Chem.* **1987**, *27*, 279. Binger, P.; Büch, H. M. *Top. Curr. Chem.* **1987**, *135*, 77. Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1. Aumann, R.; Uphoff, J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 357.

(2) (a) Reviews: Berson, J. A. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980, p 311. Gajewski, J. J. *Hydrocarbon Thermal Isomerizations*; Academic Press: New York, 1981. (b) Creary, X.; Mehrsheikh-Mohammadi, M. E.; McDonald, S. *J. Org. Chem.* **1989**, *54*, 2904 and references therein.

(3) (a) Diradical transition state hypothesis: Buchwalter, S. L. *Tetrahedron* **1984**, *24*, 5112. (b) A concerted transition state located with ab initio SCF/6-31G* and MP2/6-31G* calculations (Skancke, A.; Schaad, L. J.; Hess, B. A., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 5315) collapses upon geometry optimization to TMM at a CASSCF level employed in this work.

(4) (a) Mazur, M. R.; Berson, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 684. (b) Lazzara, M. G.; Harrison, J. J.; Rule, M.; Hilinski, E. F.; Berson, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 2233. (c) For an excellent account of the problems in the MCP rearrangements, see: Salinaro, R. F.; Berson, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 2228.

(5) (a) Yamago, S.; Nakamura, E. *J. Am. Chem. Soc.* **1989**, *111*, 7285. (b) Yamago, S.; Nakamura, E. *J. Org. Chem.* **1990**, *55*, 5553.

(6) See the supplementary material.

(7) The precision of NMR measurements precludes investigation of the isotope effects.

(8) (a) Ullmann, E. F. *J. Am. Chem. Soc.* **1960**, *82*, 505. Chesick, J. P. *J. Am. Chem. Soc.* **1963**, *85*, 2720. Gajewski, J. J. *J. Am. Chem. Soc.* **1971**, *93*, 4450. (b) LeFevre, G. N.; Crawford, R. J. *J. Org. Chem.* **1986**, *51*, 747 and references therein. (c) For the rearrangement of monoalkoxy MCPs: Baldwin, J. E.; Ghatlia, N. D.; Lundbäck, M. O. *Acta Chem. Scand.* **1987**, *B41*, 698. Kirmse, W.; Murawski, H.-R. *J. Chem. Soc., Chem. Commun.* **1977**, 122.

(9) Cf.: Wilson, R. M.; Geiser, F. *J. Am. Chem. Soc.* **1978**, *100*, 2226.

(10) For CIDNP in TMM chemistry, see: Corwin, L. R.; McDaniel, D. M.; Bushby, R. J.; Berson, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 276.

(11) The [3 + 2] cycloaddition[5a] to dimethyl fumarate (solvent) and the label scrambling proceeded at a comparable rate.

0002-7863/91/1513-3183$02.50/0